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Edited by

**David K. Larue**
Department of Geology, University of Puerto Rico
Mayagüez, PR 00708, Puerto Rico

and

**Grenville Draper**
Department of Geology, Florida International University
Miami, FL 33199
U.S.A.

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# ORIGIN AND GEOLOGIC IMPLICATIONS OF DIAGENETIC LIMESTONE IN FAULT ZONES OF BARBADOS

Rudolph Torrini, Jr.
Woodward-Clyde Consultants
5055 Antioch Road
Overland Park, Kansas 66203

Robert C. Speed
Department of Geological Sciences
Northwestern University
Evanston, Illinois 60201

George E. Claypool
Mobil Research and Development
1377 Midway Road
Dallas, Texas 75244-4312

## ABSTRACT

Fault zones and mud diapirs that crop out on Barbados Island in the crestal zone of the Barbados accretionary prism contain nodules and crusts of diagenetic limestone, limestone chimneys, molluscan fossils, and probable fossil tube worm casts. The limestone is only in fault zones that formed or were reactivated during the late (Miocene-Pliocene) history of the prism and is $^{13}C$-depleted relative to marine carbonate sediments and seawater. Geologic and isotopic evidence exists for both gaseous and nongaseous petroleum precursors to the light limestone nodules. Overthrust outer forearc basin strata of the Oceanic allochthon provided a relatively impermeable seal to upward migrating fluids. The fault zones and diapirs were evidently the preferential pathway of fluid advection and escape. The association of the diagenetic limestone with limestone chimneys, molluscan fossils, and probable fossil tube worms suggests the emergence of fault zones at the seabottom and the existence of fluid escape vents like those at modern active margins. A thermogenic origin of the hydrocarbon is indicated, with source depths ranging from 3 to 20 km. Thus, hydrocarbon source rocks could include both shallow offscrape and deeper underplated rocks. Geologic and isotopic data suggest precipitation of limestone at low temperatures (5°-29°C) and shallow depths, perhaps at or near the seabottom. The occurrence of petroleum-derived carbonates in mud diapirs as well as fault zones suggests that fluid overpressure and advection of hydrocarbons may have been linked. Migration of hydrocarbons may have been induced or enhanced by water released during the smectite-illite transformation within overpressured rocks at depth.

## INTRODUCTION

Fault zones and mud diapirs that crop out on Barbados Island in the crestal zone of the Barbados accretionary prism (Fig. 1A) contain nodules and crusts of diagenetic limestone, limestone chimneys, molluscan fossils, and probable fossil tube worm casts. The limestone is only in fault zones that formed or were reactivated during the late (Miocene-Pliocene) history of the prism and is $^{13}C$-depleted relative to marine carbonate sediments and seawater. Its stable isotopic compositions and associated hydrocarbon residues provide important constraints on sources, source depths, temperatures, and principal migration paths of advecting fluids within the Barbados accretionary prism. In this paper, we describe the petrography, mineralogy, and stable carbon and oxygen isotopic compositions of the diagenetic limestone and discuss the geologic implications of the limestone for the defluidization processes within the Barbados accretionary prism. A companion paper (Torrini et al., 1990) describes early diagenetic carbonate that occurs in terrigenous and hemipelagic strata in the basal complex of Barbados.

43 samples of diagenetic limestone were collected from various fault zones and diapirs in the Scotland District of Barbados (Fig. 1B). The mineralogy of individual samples was determined by powder X-ray diffraction (XRD) using quartz as an internal standard, and separates of all powdered samples were analyzed at the U. S. Geological Survey, Lakewood, Colorado for carbon and oxygen isotopic composition. Standard isotopic analysis techniques were used, and data for both oxygen and carbon are presented in the normal $\delta$ notation with reference to the PDB standard.

## GEOLOGY OF BARBADOS

The island of Barbados exposes the structural high of the accretionary prism of the active Lesser Antilles forearc (Fig. 1A) (Speed and Larue, 1982; Speed, Westbrook et al., 1984). The Scotland District of Barbados (Fig. 1B) is an erosional window through Pleistocene reef that caps the majority of the island. Outcrop and well studies indicate the existence of three major tectonic units beneath the reefcap (Fig. 1B) (Speed, 1988 and references therein). The highest unit is the Oceanic allochthon, whose beds were thrust east above the prism's structural high from the adjacent forearc basin. The Oceanic beds consist of terrigenous-free successions of lower bathyal-abyssal pelagic strata, mainly smectite-nanno-rad-foram marl and radiolarian mudstone, and interbedded volcanogenic turbidites and waterlaid tuffs that range in age from early middle Eocene to early middle Miocene (Torrini, 1988; Torrini et al., 1985). The intermediate unit is sporadically occurring prism cover of Miocene and possibly Oligocene age (Speed, 1988). The lowest unit is the basal complex, which is an assemblage of fault-bounded packets of terrigenous submarine fan and hemipelagic strata of probable early to late Eocene depositional age. The basal complex, which forms the foundation of the structural high of the accretionary prism and extends to depths ≥4 km, is thought to have formed by offscrape and accretion in late Eocene time. Organic carbon-rich mud diapirs cut the basal complex (Larue and Speed, 1984) and locally, the Oceanic allochthon (Torrini et al., 1985; Larue, 1988). The diapirs consist of angular blocks of sedimentary rocks from sand to 100 m sized, green mudstone granules, and foliated organic carbon-rich sandy mudstone matrix.

Evidence for modern emergence of fluids from the structural high of the prism include: (1) mud diapirs on and around Barbados (Torrini and Speed, 1989), (2) oil seeps from fault zones on Barbados, and (3) melt breccias on Barbados that indicate combustion around local vents of hydrodarbon gas.

## DIAGENETIC LIMESTONE

The diagenetic limestone described in this paper occurs exclusively within organic carbon-rich mud diapirs and fault zones, including *intra-Oceanic fault zones* (OFZ) that separate nappes of Oceanic beds

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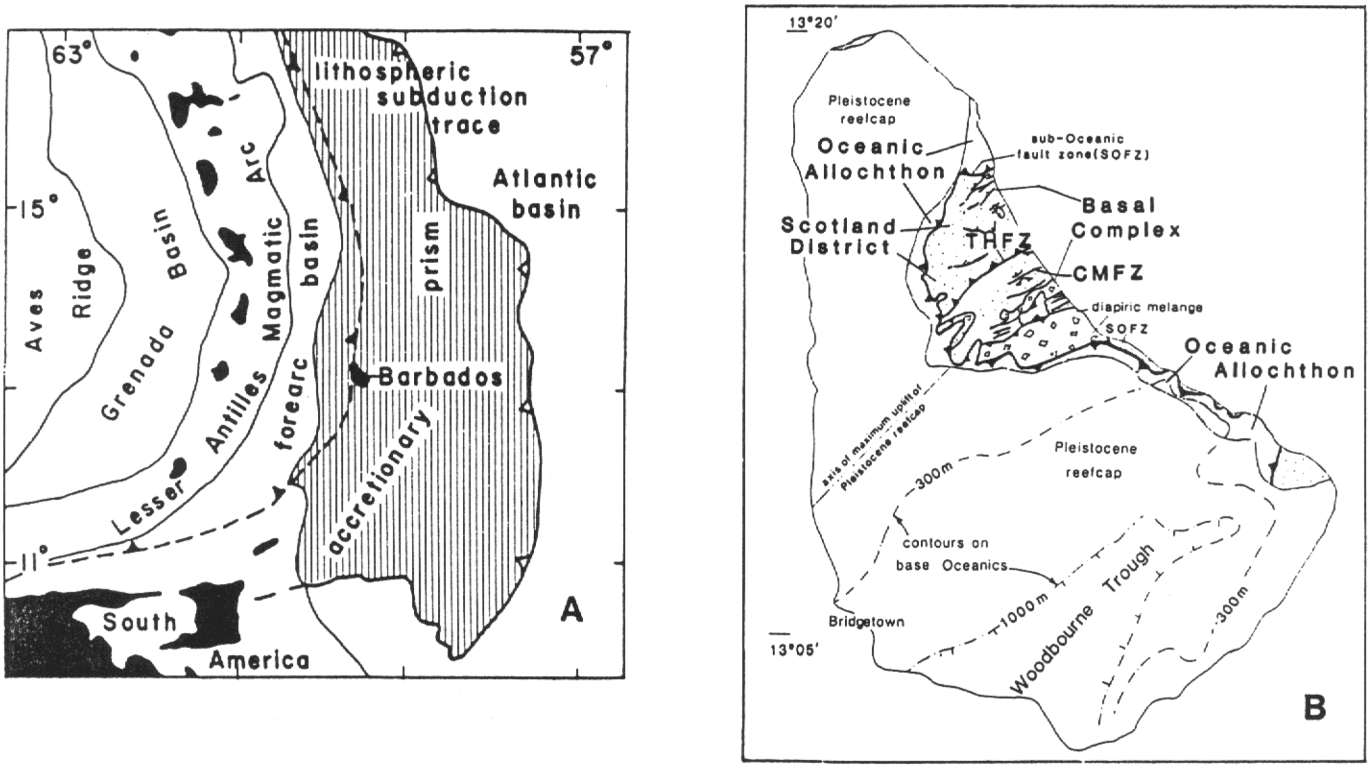


Figure 1. A) Index map showing location of Barbados Island at structural high of Lesser Antilles forearc; B) Generalized geologic map showing major tectonostratigraphic units of the Scotland District of Barbados. SOFZ, Sub-Oceanic Fault Zone; CMFZ, Chalky Mount Fault Zone; THFZ, Turner Hall Fault Zone.

within the Oceanic allochthon, the *sub-Oceanic fault zone* (SOFZ), which is the sole fault of the Oceanic allochthon, and *reactivated fault zones within the basal complex*, including the Turner Hall fault zone (THFZ) and the Chalky Mount fault zone (CMFZ) (Fig. 1B). The OFZ and SOFZ are semitabular zones of variable thickness that consist of one or more discrete striated fault surfaces whose walls contain foliated clay-rich insoluble residues that are relics from dissolution of carbonate in Oceanic beds. Motions in the OFZ and SOFZ are no older than Miocene, the age of emplacement of the Oceanic allochthon according to paleontological constraints (Speed, 1988). Reactivated fault zones of the basal complex are distinguished by the existence of late structures that represent departures from early kinematics and apparently reflect late intraprism contraction (Speed, 1983). The age of reactivation of the CMFZ is unknown, but renewed motion on the THFZ probably includes Miocene and (or) Pliocene components. Displacements in the above mentioned fault zones were taken up under shallow, brittle conditions, resulting in the formation of cleavage, microfractures, and broken formation that clearly increased the permeability of fault zone rocks relative to wall rocks.

The main features of the limestone nodules and crusts are their occurrence as discrete bodies and evidence for a diagenetic rather than depositional or biostromal origin. The limestone bodies are composed strictly of calcite. They are sharply bounded but are variably tabular to equant, centimeter to several meters in length, and dispersed or concentrated. Most are massive, but some contain relict sedimentary lamination. In fault zones, limestone nodules are commonly aligned in horizons that parallel the local fault zone boundaries (Torrini et al., 1985). Fault zones at several localities include limestone chimneys, molluscan limestone, and limestone tubes in sinuous, intertwined clusters (Larue and Suess, 1985; Speed et al., 1985). The limestone chimneys are evidence of ancient fluid escape at seabottom vents, and the molluscan limestone and limestone tubes are interpreted as associated vent-based benthic communities (mollusks, tube worms). Thus, at least part of the diagenetic limestone is thought to have precipitated at or near the sediment/water interface.

Four different diagenetic textures are recognized amongst the limestone: (1) radiaxial calcite in replacive radiating sheaves (microcabbageheads) and in microveinlets, often in cross-cutting sets, (2) pore-filling blocky calcite, (3) replacive micritic calcite, and (4) replacive rhombohedral calcite. Two or more of the textures commonly occur within a single specimen. Precursor material, preserved in vanishing to moderate quantities, includes quartz, feldspar, clay, siliceous tests, and solid organic substances. Calcareous biogenic particles are generally absent. Masses of diagenetic calcite locally cross-cut and replace foliated fault zone rock, clearly indicating that limestone precipitation was syn- or post-faulting.

The preferential occurrence of isotopically light limestone in the SOFZ, OFZ, and reactivated fault zones of the basal complex suggests that fluid migration and limestone precipitation were genetically related to late intraprism contraction and emplacement of the Oceanic allochthon in Neogene time. Thus, limestone precipitation probably began no earlier than early Miocene. Limestone nodules in mud diapirs may be fault-zone related protoliths or diagenetic products of hydrocarbon degassing during diapirism. Such diapirism is thought to have occurred at least partly since early Miocene time (Larue and Speed, 1984; Speed, 1988). It may have been generally coeval with contraction and uplift in the crestal zone of the prism and with the Neogene reactivation of old accretionary surfaces in the basal complex and emplacement of the Oceanic allochthon.

## ISOTOPIC COMPOSITIONS AND INTERPRETATIONS

The $\delta^{13}C$ and $\delta^{18}O$ values of the diagenetic limestone range from -15.1 and -54.5 o/oo and -1.42 to +2.12 o/oo (PDB), respectively (Fig. 2). The $\delta^{13}C$ compositions are atypical of marine carbonate sediment and indicate that the carbon in the calcite is at least partly organic. Approximately one third of the $\delta^{13}C$ values are lighter than those of carbon of nongaseous organic material (-21 to -28 o/oo), indicating a concribution of carbon from hydrocarbon gases, presumably methane. The confined occurrence of isotopically light limestone to fault zones and diapirs suggests that the methane migrated along fault zones and diapiric pathways from depth and was not a stratiform accumulation generated by shallow, in situ bacterial decay of organic matter. Geologic and isotopic evidence exists for both gaseous and nongaseous petroleum precursors to the light limestone nodules, and the majority of $\delta^{13}C$ values are inconsistent with inorganic carbon precursors. The methane source was probably mainly thermogenic, not biogenic because the compositional range of the limestone nodules does not include any $\delta^{13}C$ values that can be uniquely attributed to a biogenic methane precursor (e.g. -75 to -90 o/oo; Rice and Claypool, 1981) and because oil seeps and asphaltic hydrocarbon residues found in certain fault zones were generated at temperatures ≥100°C.

Because of geologic evidence for precipitation of at least part of the limestone around ancient seabottom fluid escape vents, the water fraction of the limestone-forming fluids may have consisted of various proportions of diagenetic pore water and sea water. The $\delta^{18}O$ value of the fluids was probably ≥ -2.0 o/oo because more negative values yield calculated equilibration temperatures colder than the minimum known temperature of bottom water (2°C; Kennett, 1982). Precipitation of the limestone is thought to have occurred in Neogene time when major glaciation certainly affected the $\delta^{18}O$ composition of the world oceans (Kennett, 1982). Accordingly, we have calculated temperatures of formation of the limestone (Craig, 1965) assuming isotopic equilibration with $\delta^{18}O$ fluid compositions of -1.2 o/oo (SMOW, nonglacial oceans; Shackleton and Kennett, 1975) ) and +1.2 o/oo (SMOW, oceans at glacial maxima; Kennett, 1982; E. Birchfield, personal communication, 1986). The calculated isotopic equilibration temperatures, which range from 5°-29°C, are relatively low, supporting our geologic interpretation that precipitation of the limestone in fault zones and diapirs occurred at shallow depths, perhaps at or near the seabottom.

The hydrocarbon-derived component of the diagenetic fluids originated from both solidified oil and methane. Estimated source depths for the oil and methane based on the temperature range for thermal catagenesis (75°-300°C) and a geothermal gradient on Barbados of 15°C/km (Larue et al., 1985) range from 3 to 20 km. This indicates that hydrocarbon source

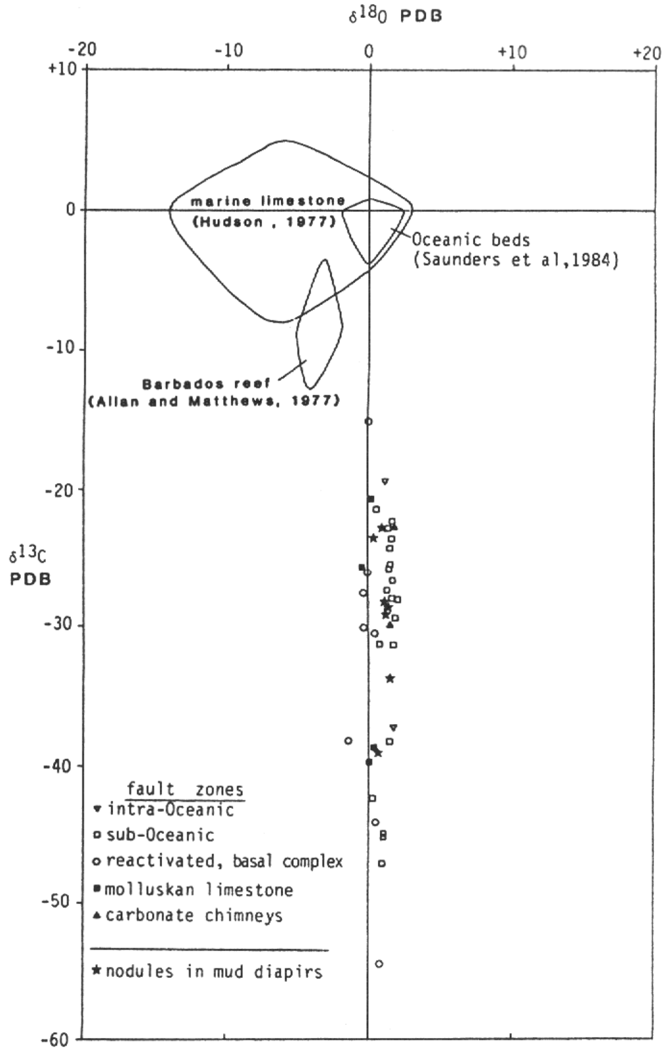


Figure 2. Stable carbon and oxygen isotopic compositions of diagenetic limestone nodules in fault zones and mud diapirs of Barbados.

rocks could include both shallow offscraped and underplated rocks at the base of the accretionary prism. Geologic and isotopic lines of evidence suggest precipitation of the limestone at relatively low temperatures (5°-29°C) and shallow depths, perhaps at or near the seabottom. Thus, potential sources of the water fraction of the diagenetic fluids are: (a) seawater that was contemporaneous with emergent faulting and (or) seabottom fluid venting, (b) shallow origin diagenetic pore water from the Oceanic allochthon or shallow levels within the prism, or (c) deep origin diagenetic pore water that cooled during advection from deeper levels within the prism. The occurrence of petroleum-derived nodules in mud diapirs as well as fault zones suggests that fluid overpressure and advection of hydrocarbons were linked. Migration of hydrocarbons may have been induced or enhanced by water released during the dehydration of expandable layer clays within overpressured rocks at depth.

Oxidation of hydrocarbons probably ocurred by one or more of the following mechanisms: 1) exposure to oxygenated seawater in the aerobic zone (≤1 m), 2)

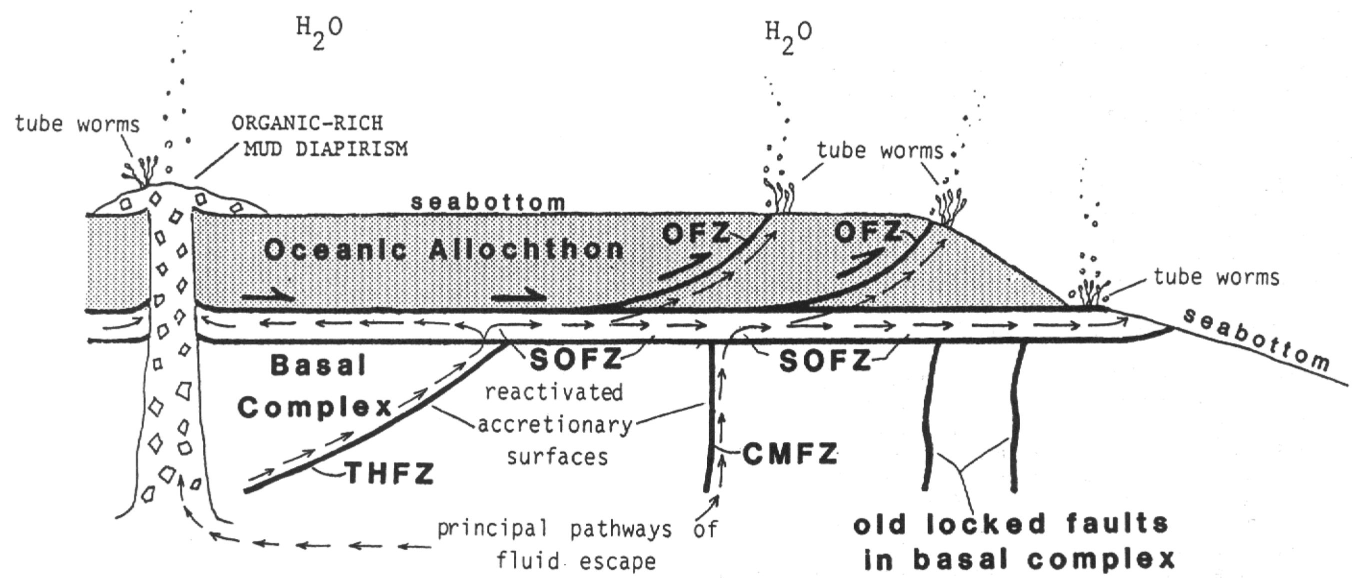


Figure 3. Schematic diagram showing principal pathways of fluid migration and escape from the crestal zone of the Barbados accretionary prism; heavy lines are faults; CMFZ, Chalky Mount Fault Zone; THFZ, Turner Hall Fault Zone; SOFZ, Sub-Oceanic Fault Zone; OFZ, Intra-Oceanic Fault Zones. Tube worms thrive at seabottom where methane-bearing fluids are expelled.

circulation of oxygenated seawater through fault zones, or 3) anaerobic bacterial processes within the zone of sulfate reduction (Hudson, 1977; Rice and Claypool, 1981). We speculate that oxidation of the hydrocarbons generated light $CO_2$ which increased the acidity of the upward-migrating fluids and led to dissolution of marine carbonate rock in fault zone walls. The consequent introduction of $HCO_3$ from calcareous wall rocks would have increased the pH, causing biogenic silica and phyllosilicates to dissolve and calcite to precipitate.

## GEOLOGIC IMPLICATIONS

Late events in the history of the accretionary prism are recorded by structures in the basal complex, Miocene prism cover, and the Oceanic allochthon. These include Neogene arcward tectonic wedging of the prism into the forearc basin succession and associated oceanward thrusting of outer forearc basin strata of the Oceanic allochthon above the prism's structural high. Such Neogene motions were accompanied by intraprism contraction by motions on reactivated faults in the basal complex and mud diapirism. During these later stages, turbiditic sandstone interbeds in the basal complex were relatively impermeable due to cementation by early diagenetic carbonate (Torrini et al., 1990). Moreover, smectite-rich beds of the overthrust Oceanic allochthon provided a relatively impermeable seal to advecting fluids of the accretionary prism. Thus, mud diapirs, reactivated fault zones of the basal complex, and the sub- and intra-Oceanic fault zones of the Oceanic allochthon were the principal pathways of fluid advection and escape from the accretionary prism (Fig. 3). Secondary (fracture) permeability was clearly important in providing an avenue for fluid escape.

A record of early (Eocene) fluid venting from the accretionary prism apparently is lacking, at least from exposures on Barbados. The petroleum-derived diagenetic limestone described in this paper occurs only in fault zones with late (Neogene) displacements. The absence of a diagenetic record of early fluid venting might be explained by: (a) erosion of shallow prism rocks that contained the early diagenetic carbonate record, (b) lack of carbonate precipitation due to trapping of methane in gas hydrate, or (c) lack of carbonate precipitation due to local anoxia that discouraged oxidation of methane for incorporation into diagenetic carbonate.

## CONCLUSIONS

Fault zones and mud diapirs on Barbados contain petroleum-derived diagenetic limestone nodules and crusts. The diagenetic limestone is only in fault zones that formed or reactivated during the late (Miocene-Pliocene) history of the accretionary prism. Fault zones and diapirs were evidently the preferential pathway of fluid advection and escape (Fig. 3). Overthrust outer forearc basin strata of the Oceanic allochthon provided a relatively impermeable seal to upward migrating fluids. The association of the diagenetic limestone with limestone chimneys, molluscan fossils, and probable fossil tube worms suggests the emergence of fault zones at the seabottom and the existence of fluid escape vents like those at modern active margins. A thermogenic origin of the hydrocarbon is indicated, with source depths ranging from 3 to 20 km. Thus, hydrocarbon source rocks could include both shallow offscrape and deeper underplated rocks. Geologic and isotopic data suggest precipitation of limestone at low temperatures (5°-29°C) and shallow depths, perhaps at or near the seabottom. The occurrence of petroleum-derived carbonates in mud diapirs as well as fault zones suggests that fluid overpressure and advection of hydrocarbons may have been linked. Migration of hydrocarbons may have been induced or enhanced by water released during the smectite-illite transformation within overpressured rocks at depth.

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